Metathesis Activity and Stability of New Generation Ruthenium Polymerization Catalysts

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ABSTRACT: A kinetic study of three ruthenium carbene catalysts, $(H_2IPr)(PCy_3)(Cl)_2Ru{=}CHPh$, **3** (investigated extensively by Mol), $(H_2IMes)(Cl)_2Ru{=}CH(o\text{-}i\mathrm{PrOC_6H_4})$, **4** (Hoveyda's catalyst), and $(H_2IPr)(Cl)_2Ru{=}CH(o\text{-}i\mathrm{PrOC_6H_4})$, **5** (a new catalyst structure), was conducted under ADMET polymerization conditions. The kinetic behavior of these catalysts was compared to the classical first- and second-generation Grubbs' complexes at 30, 45, and 60 °C. Complex **3** exhibits the highest initial ADMET rate (80 DP s^{-1}) of any phosphine complex to date and efficiently promotes metathesis even at temperatures as low as 0 °C. Complex **4** alone does not polymerize 1,9-decadiene in the bulk; however, addition of a polar solvent induces polymerization. Combining elements of catalysts **3** and **4** yielded the new complex **5**. This complex results in higher polycondensation rates than previous Hoveyda-type structures and exhibits an increased stability over its parent phosphine complex. The new catalyst polymerizes 1,9-decadiene in the bulk to high polymer (M_n = 40 000 g/mol) using low catalyst loadings (0.1 mol %). The isomerization chemistry induced by complexes **3** and **5** was investigated using a model compound, 1-octene.

Introduction

The recent development of ruthenium carbene complexes (Figure 1) has increased considerably the utility of olefin metathesis in the fields of both organic synthesis and polymer chemistry. The introduction of the well-defined, functional group tolerant complex $(PCy_3)_2(Cl)_2Ru{=}CHPh$ **(1)** by Grubbs and co-workers[1] stimulated researchers' interest toward late-transition-metal-catalyzed metathesis chemistry, for it is a useful catalyst in a variety of ring-closing metathesis (RCM), cross-metathesis (CM), acyclic diene metathesis polymerization (ADMET), and ring-opening metathesis polymerization (ROMP) reactions.[2] Improvements on this "first-generation" ruthenium structure have been reported by many groups in recent times. For example, the Grubbs research group reported that incorporation of the more bulky and strongly σ-donating imidazolylidene ligand leads to higher activity and thermal stability, enabling the preparation of α-functionalized di-, tri-, and tetrasubstituted olefins.[3] These imidazolylidene-based catalysts behave in a manner similar to that of early transition metal catalysts such as Schrock's molybdenum catalyst (**6**)[4] and remain active at loadings as low as 0.05 mol % for RCM and 0.0001 mol % for ROMP.[5]

Additional ligand variations have led to further improvements in both catalytic activity and stability. For example, Mol and co-workers reported improved turnovers during the cross-metathesis of terminal olefins with a modified version of the imidazolylidene ligand, catalyst $(IPrH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3**), first synthesized by Fürstner.[6] Also, Hoveyda et al. have developed the complex $(H_2IMes)(Cl)_2Ru{=}CH(o\text{-}i\mathrm{PrOC_6H_4})$ (**4**) which promotes olefin metathesis by a unique "release−return" mechanism, allowing efficient metal recovery without significant loss of activity.[7] In fact, complex **4** can readily be used in combinatorial synthesis in air with reagent-grade solvents. This Ru complex offers reactivity and chemo- and stereoselectivity profiles differing from both catalysts **1** and **2**, notably during the metathesis of electron-deficient olefins.[8] The robustness of this complex also allows its use in solid-supported heterogeneous catalysis.[8e]

Acyclic diene metathesis (ADMET) chemistry has enjoyed the benefit of this metathesis catalyst research, resulting in the synthesis of unique architectures and new functionalized materials,[9] such as perfectly branched polyethylene[9a,g] and amino acid-containing polyolefins.[9b,c] The choice of catalyst to perform these transformations is dictated by the monomer structure and the reaction conditions. For example, Schrock's catalyst is best used for hydrocarbon dienes and some functionalized olefins, whereas Grubbs' catalysts are preferred with highly functionalized monomers and at higher temperatures. ADMET, CM, and RCM require longer reaction times than ROMP chemistry, and so catalyst entities with longer lives are preferred. Consequently, our group has a particular interest in complexes that exhibit both long lifetimes and high turnovers ratios. We have prepared a new catalyst structure (complex **5**) by combining the thinking that yielded the Grubbs, Hoveyda, and Mol complexes, and we find that this ADMET catalyst exhibits improvements in terms of its stability.

We have used a kinetic approach to investigate the activity and utility of these ruthenium complexes during ADMET polymerization, work which has led to the design of more efficient ADMET catalyst systems.[10] Previously, we reported a comparative kinetic study of Grubbs' catalysts **1** and **2** during the ADMET polymerization of the benchmark monomer, 1,9-decadiene, research that showed the effect of temperature on activity and initiation rates.[11] Catalyst **2** is clearly more active if used at temperatures of 45 °C and above. The olefin isomerization activity of catalysts **1** and **2** was investigated as well,[12] where catalyst **2** was found to isomerize both external and internal olefins if used at

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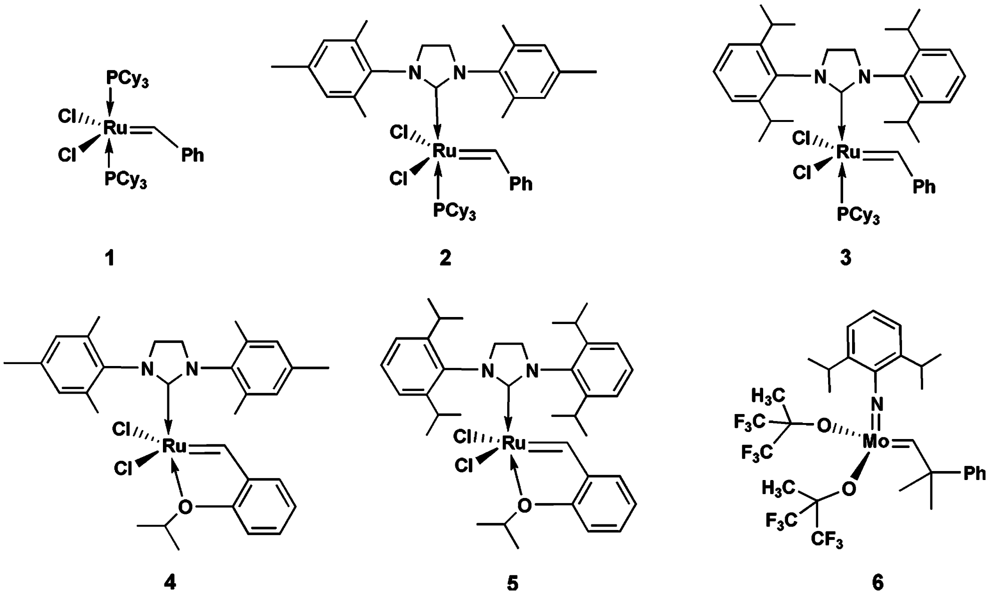

Figure 1. Metathesis catalysts.

Table 1. Initial Rates for Complexes 1−5 during the ADMET Oligomerization of 1,9-Decadiene

catalyst	monomer:catalyst ratio	initial rate (10^{-3} DP s^{-1}) 30 °C	45 °C	60 °C
1[a]	450:1	1.0 ± 0.5	2.3 ± 0.4	5.1 ± 0.6
2[a]	450:1	0.42 ± 0.05	4.4 ± 0.7	23 ± 3
3	450:1	36 ± 1	39 ± 7	55 ± 10
3	900:1	8.8 ± 4.0	39 ± 1	78 ± 10
4	450:1	4.8 ± 3	18 ± 5	
5	450:1	12 ± 2	42 ± 4	68 ± 10

[a] Data obtained from ref 11.

its optimal temperature for ADMET, 60 °C. This observation is important to consider when building precise polymer microstructures.

In this paper we expand upon our earlier kinetic work to include complexes **3**, **4**, and the new complex **5**, comparing them with the first- and second-generation Grubbs' catalysts.[11] Initial rates of ADMET polymerization were measured at different temperatures, and the stability and activity of these complexes were examined at longer reaction times. Finally, we investigated their propensity to induce olefin isomerization under polycondensation conditions.

Results and Discussion

Kinetic Assessment of Catalyst Activity. ADMET polycondensation of α,ω-dienes releases ethylene as the condensate, the volume of which can be measured and used to calculate the average degree of polymerization (DP) of the monomer as a function of time. The kinetic experiments were run for approximately an hour, focusing on the oligomerization (not polymerization) of the monomer. The monomer 1,9-decadiene was chosen in this study because of its well-understood behavior during ADMET chemistry. Monitoring oligomerization by plotting DP vs time allows for an efficient method to compare the catalytic activity for various complexes. Table 1 displays the initial rates of 1,9-decadiene ADMET chemistry, calculated as the initial slope (DP vs time) of each kinetic curve during the average dimerization (DP = 2) of the monomer.

Catalytic activity was measured at three temperatures (30, 45, and 60 °C) and two catalyst loadings (450:1 and 900:1 monomer:catalyst), providing a broad basis set to evaluate the catalyst systems tested. This activity was compared to the widely used first- and second-generation ruthenium catalysts, previously examined in ADMET conversions by our group.[11]

The kinetic runs at 30 °C show that the Mol catalyst, complex **3**, exhibits the highest activity of any ruthenium complex to date in the dimerization of 1,9-decadiene. Figure 2 illustrates these data. When compared to the benchmark catalyst **1**, complex **3** shows a 36-fold increase in activity at 30 °C (see Table 1). This low-temperature activity makes catalyst **3** an ideal candidate for controlled organic synthesis and polymerization applications. Further, the initial dimerization rate when using complex **3** is greater than either complex **1** or **2** at both 45 and 60 °C. For example, complex **3** affords a dimerization rate of 55×10^{-3} DP s^{-1}, twice that when using complex **2** at 60 °C; in fact, the high activity of complex **3** at 60 °C makes it difficult to accurately measure the evolution of ethylene, resulting in a large error in the measured DP.

This higher activity of complex **3** most likely originates from the increased steric bulk around the ruthenium center, a result of the isopropyl groups present on the ligand. Apparently, the interaction of the isopropyl groups with the carbene fragment and/or the chloro groups allows for faster and earlier dissociation of the tricyclohexylphosphine, which has been commonly accepted as the initial rate-determining step of the metathesis reaction. This statement can be confirmed by comparing the ^{31}P NMR spectrum of complex **3** vs that of either complex **1** or **2**. The phosphine resonance is shifted from 32 ppm for **2** to 28.1 ppm for **3**, where this upfield shift indicates a weaker Ru−P bond, implying an easier dissociation of the phosphine. Also, the induction period observed with **2** is not observed with **3**, which is consistent with complex **3**'s faster phosphine dissociation. The induction period is thought to correspond to the initial dissociation of phosphine before the steady-state concentration of the 14-electron (e^-) ruthenium alkylidene complex is reached.

While complex **3** shows the largest decadiene dimerization rate for any complex to date, increasing temperature has an adverse effect on the lifetime of

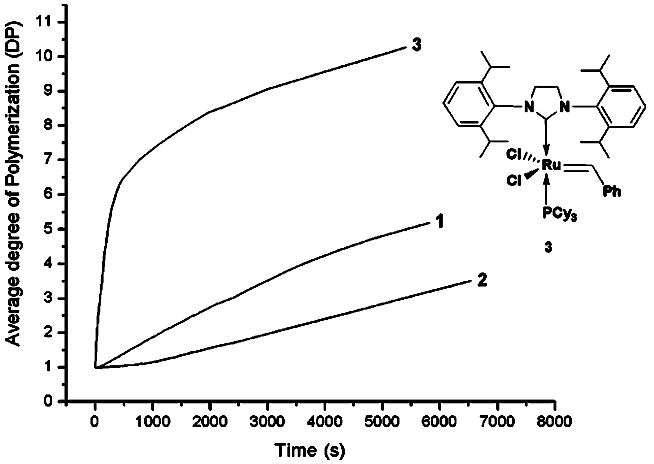

Figure 2. DP vs time curves for complexes **1**−**3** using 450:1 monomer:catalyst ratio at 30 °C.

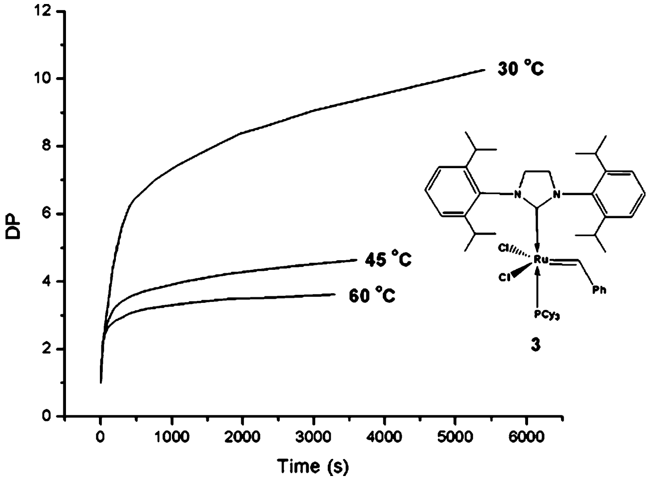

Figure 3. Comparison of the activity of complex **3** at three different temperatures using a 450:1 monomer:catalyst ratio.

the catalyst (Figure 3). Complex **3** no longer competes with either **1** or **2** at temperatures above 45 °C beyond trimerization of 1,9-decadiene. Figure 4 further illustrates this phenomenon; these lower turnovers were also reported by Mol at elevated temperature.[6] This decrease in conversion likely is due to the thermal decomposition of the complex as observed with Grubbs' catalysts[13] or by way of C−H and/or C−C activation pathways.[14] Decomposition may occur faster with complex **3** due to the presence of an electron-rich methine proton on the isopropyl groups, which would be more likely to undergo C−H activation than the methyl protons of complex **2**. Moreover, the additional carbons on each isopropyl group may increase the probability of insertion of the ruthenium into the C−C bond.

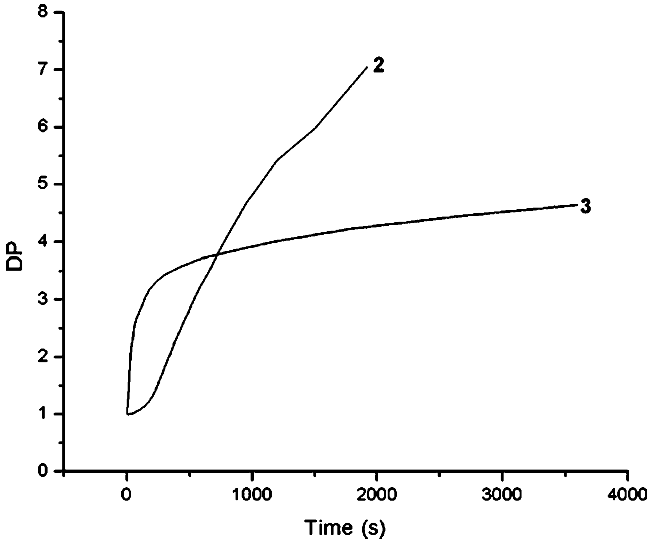

Figure 4. DP vs time curves for complexes **2** and **3** using 450:1 monomer:catalyst ratio at 45 °C.

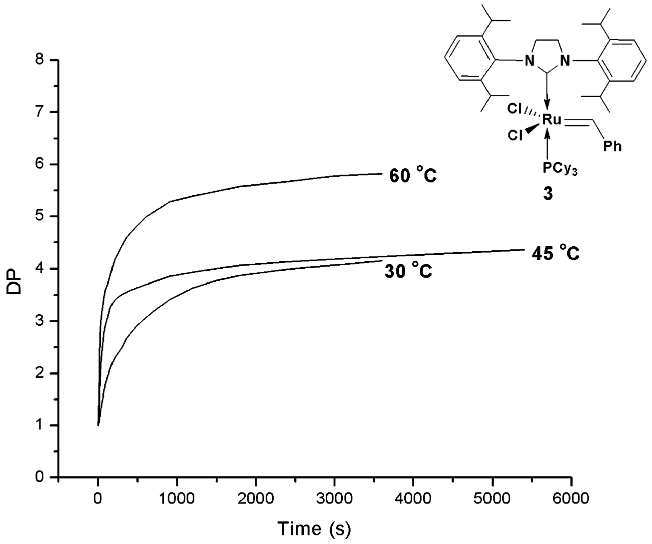

Figure 5. DP vs time data for complex **3** using 900:1 monomer:catalyst ratio.

On the other hand, this temperature trend is inverted when the monomer-to-catalyst ratio is doubled (Figure 5). Indeed, higher conversions are reported when the temperature is increased from 30 to 60 °C with its average DP reaching 4 and 5.8, respectively. In addition, complex **3** is more active initially at 60 °C when using lower catalyst ratios; the data are reported in Table 1. For example, when the catalyst concentration is decreased by a factor of 2, the respective rate increases from 55 × 10^{-3} to 78 × 10^{-3} DP s^{-1}. The increase in the overall activity observed at high temperature suggests that less catalyst decomposition occurs. This decrease in the decomposition rate when the catalyst concentration is lower supports a bimolecular decomposition pathway.[13] However, at this point we cannot rule out the possibility of an internal decomposition as outlined above. More likely, this would prove the coexistence of both mechanisms. Further, the reaction rate for complex **3** at 30 °C is decreased by a factor of 4, which is consistent with the lower catalyst ratio as little decomposition should occur at such low temperatures. Besides, this activity trend has been reported by Mol as well in the dimerization of terminal olefins.[6]

Although known for its particular tolerance to a variety of substrates,[8] complex **4** appears to be unstable once dissolved in 1,9-decadiene, for complex **4** affords low conversions at 30 and 45 °C (Figure 6). Consequently, no experiment was conducted at 60 °C with complex **4**.

The low stability of complex **4** may be attributed to its release−return mechanism, yielding an unstable 14 e^- species by the loss of isopropoxystyrene, which in turn produces the unbound ligand and/or its subsequent attachment to the chain end. We assume that the low stability of complex **4** is due to this highly unstable 14 e^- intermediate not being restabilized by the isopropoxy

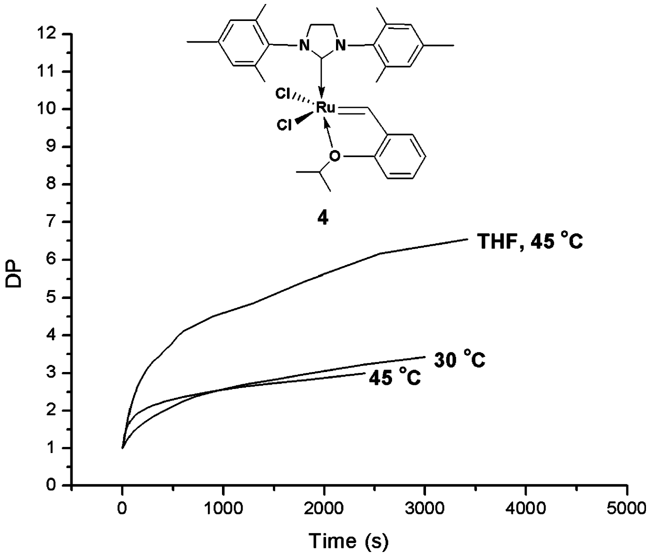

Figure 6. DP vs time data for complex **4** using 450:1 monomer:catalyst ratio.

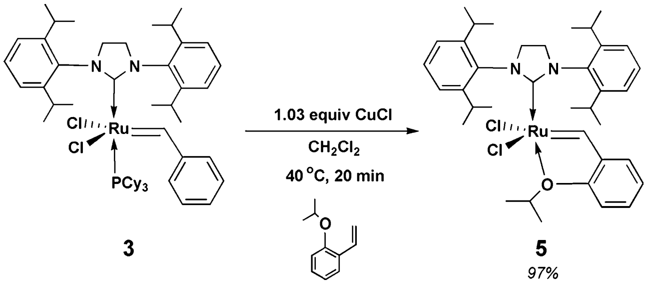

Figure 7. Synthesis of complex **5**.

ligand. This $14\ e^-$ complex may have to be stabilized by coordination to the substrate (monomer) or solvent, and since 1,9-decadiene lacks any kind of electron donor or Lewis basic group, it is not able to serve as a stabilizing ligand. Consequently, the catalyst apparently decomposes immediately after activation. To verify this assumption, we conducted the same experiment adding a catalytic amount of THF to the bulk reaction mixture, and as is apparent in Figure 6, a drop of THF improved the activity of complex **4** when polymerizing 1,9-decadiene. These data refute the general belief that ruthenium catalysts exhibit lower metathesis activity in THF.[15] In this case, THF must stabilize the complex just enough to make it viable for metathesis instead of forming a stable complex as it is the case for phosphine-ligated catalysts.

These observations led us to synthesize complex **5**, which in effect combines the thinking of Grubbs, Mol, and Hoveyda. The complex was obtained in good yields by implementing the same synthetic procedure used to generate complex **4**,[7] simply substituting complex **3** as one of the starting compounds (Figure 7). Conveniently, **5** can be purified in the air, affording a dark green crystalline solid after flash chromatography and precipitation in hexane, where the copper–phosphine complex must be removed by filtration prior to column chromatography. The activity of this new complex was evaluated using the same kinetic study as done previously with 1,9-decadiene.

Contrary to its predecessor **4**, complex **5** catalyzes the ADMET oligomerization of 1,9-decadiene, as shown in Figure 8. The shape of the kinetic curves is the same as observed for the parent complex **3**, and the overall

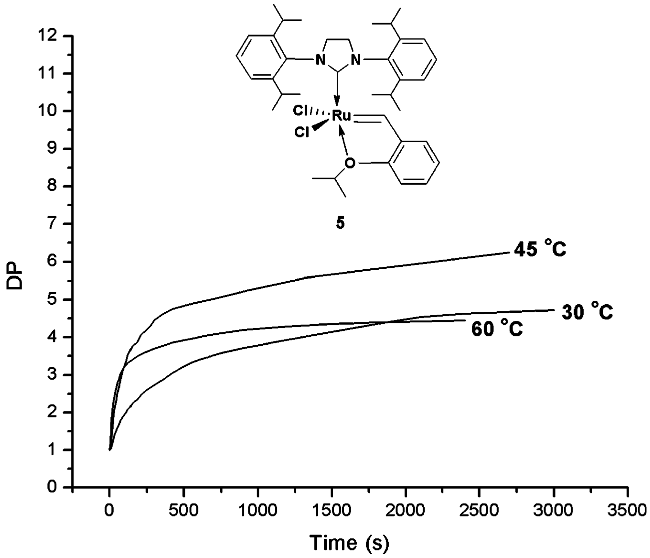

Figure 8. DP vs time data for complex **5** using 450:1 monomer:catalyst ratio.

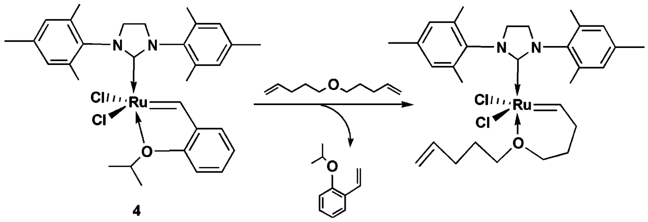

Figure 9. Proposed intermediate of complex **4** during the metathesis of dipentenyl ether.

activity is less a function of temperature. There is no definite trend, but 45 °C seems to be an optimal temperature. On the other hand, the initial oligomerization rate when using complex **5** is more sensitive to temperature variations than it is for catalyst **3**, reaching a maximum of 68×10^{-3} DP s^{-1} at 60 °C. Thus, higher temperatures are recommended to get fast initiation using this particular complex. Moreover, catalyst **5** exhibits faster initial rates than **4**, which is consistent with the introduction of the bulkier isopropyl groups on the imidazolylidene ligand. In fact, complex **5** produces high molecular weight poly(octenamer) whereas complex **4** only yields oligomers, even after 120 h in the bulk.

Interestingly, complex **5** does not need THF to catalyze the ADMET reaction of 1,9-decadiene. To better understand the differences between catalysts **4** and **5** and the role of polar reaction conditions on these Hoveyda-type catalysts, kinetic experiments were completed using dipentenyl ether as the monomer instead of 1,9-decadiene. Dipentenyl ether was chosen for its inherent electron-donating ability; it serves as both monomer and solvent, possibly allowing coordination to stabilize the reactive intermediate through a six-membered ring transition state (Figure 9).

Surprisingly, the activity of complex **4** with dipentenyl ether is actually lower than with 1,9-decadiene using the same kinetic conditions, suggesting that dipentenyl ether intramolecular complex is not sufficiently labile to allow coordination of other monomer molecules, thereby preventing further continuation of the metathesis process. Experiments conducted using complex **5** (Figure 10) also show a decreased activity of about 1 DP s^{-1} where the initial rate drops from 42×10^{-3} DP

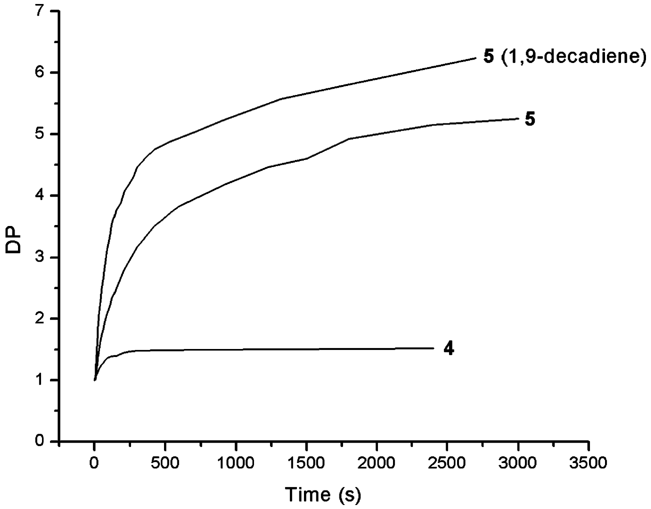

Figure 10. DP vs time data for complexes **4** and **5** using dipentenyl ether as the monomer (450:1 monomer:catalyst).

s^{-1} (1,9-decadiene) to 15 × 10^{-3} DP s^{-1} (dipentenyl ether). The fact that a similar behavior was obtained with both complexes **4** and **5** suggests that these Hoveyda-type systems are sensitive to substrate polarity and may give better results in solution with solvents of lower polarity. Another possibility could be that this particular ether is too sterically hindering to effectively stabilize the Ru center.

Overall, **5** is a better catalyst than **4** for the ADMET oligomerization of either 1,9-decadiene or dipentenyl ether, although slightly less active toward the ether monomer. Considering the hypothesis of a 14 e^- intermediate as proposed for the parent complex **4**, the enhanced activity of **5** can be explained in terms of olefin affinity. The isopropyl groups of the imidazolylidene should exert a stronger steric pressure on the carbene moiety and favor the formation of a metallacyclobutane with the incoming olefin. The inherent olefin affinity offers an ideal stabilization to the 14 e^- intermediate and could account for the higher activity. The crystal structure of **5**[16] shows that the Ru−O is shorter, meaning the coordination of the oxygen to the ruthenium is stronger than in complex **4**.[7] Therefore, the increased stability of **5** could be due to a higher tendency of the isopropoxystyrene to come back and stabilize the 14 e^- intermediate. While the activity of complex **5** at low conversion does not compete with the activity of complex **3**, its long-term stability, described below, renders it an attractive metathesis catalyst.

Thermal Stability of the Catalysts. The decomposition rates of complexes **3** and **5** were monitored by ^{1}H NMR in d_6-benzene at 55 °C and calculated as the time for half the complex to decompose. As observed during the kinetic study, complex **3** is not resistant to high temperatures, exhibiting a half-life of 90 min at 55 °C. On the contrary, complex **5** remains completely intact at 55 °C for more than 3 days, showing no sign of decomposition whatsoever (Table 2). This complex is stable not only in air but also in solution even at elevated temperatures. This increased stability is desirable for RCM, CM, and ADMET chemistry in solution and may also be useful for solid-state ADMET polymerization.[17]

Further Comments on ADMET Polymerization. To expand these kinetic oligomerization measurements made using 1,9-decadiene, we investigated the utility of the complexes during full-scale polymerization of this monomer. These polymerizations were conducted using standard Schlenk techniques, with complexes **3** and **5** at 55 °C using both 450:1 and 900:1 monomer:catalyst ratios (Table 3). The resultant poly(octenamer)s were characterized by ^{1}H and ^{13}C NMR and further analyzed by GPC and DSC. Molecular weights were compared to poly(octenamer)s obtained with the catalyst systems **1**, **2**, and **6**.

Table 2. Half-Lives for the Decomposition of Complexes 3 and 5

complex	temp, °C	concn, M	half-life
1[a]	55	0.023	8 days
3	55	0.032	90 min
5	55	0.032	>3 days

[a] Value taken from Grubbs et al.[1a]

Table 3. Polymerizations of 1,9-Decadiene at 55 °C for 120 h

catalyst	monomer:catalyst ratio	M_n (g/mol)	PDI
1	450:1	12 000	1.8
2	450:1	78 000	1.8
Schrock (**6**)	1200:1	15 000	1.7
3	450:1	29 000	1.6
3	1000:1	37 000	1.9
5	450:1	21 000	1.6
5	1000:1	32 000	1.6

When the polymerizations were heated at 55 °C for an extended period, poly(octenamer) was obtained with M_n of 37 000 g/mol using complex **3** and 32 000 g/mol using complex **5**. This is an encouraging result, as the benchmark Shrock's molybdenum catalyst (**6**) for ADMET polymerization produces a polymer half that average mass, or M_n = 15 000 g/mol poly(octenamer) under the same conditions. Both are acceptable molecular weights in step polymerization chemistry, especially for functionalized versions of polyolefins made by this route. End-group conversion increases from 99.1% to 99.6% in this doubling of molecular weight, clearly illustrating how clean mechanistic chemistry is essential in any step polymerization. Further, the use of complex **3** or **5** leads to successful polymerization with lower catalyst loadings (0.05 mol %).

Complex **4** was not included in this polymerization study since initial experiments at 30 °C in the bulk produced only oligomeric poly(octenamer), an observation consistent with the model kinetic study. The situation may differ when polymerizing functionalized diene monomers in THF, however. This research is underway.

Isomerization of the Olefin Bond. Olefin isomerization is a major side reaction of Ru-catalyzed metathesis; however, the specie(s) responsible for such transformation, whether it is a decomposition product or the metathesis catalyst itself, have not been fully identified yet.[12,18] Studying isomerization therefore occupies a significant part in the process of understanding catalyst decomposition. Besides, since part of our research focuses on precision in polymer synthesis, we have explored in detail the isomerization activity of complexes **3** and **5**, realizing that olefin isomerization generates macromolecules containing less well-defined polymer structures. The isomerization study was done using a model compound, 1-octene, as the starting reagent. Typical results are illustrated in Figure 11, demonstrating that both complexes **3** and **5** isomerize the olefinic bonds in the reactant as well as in the metathesis products.

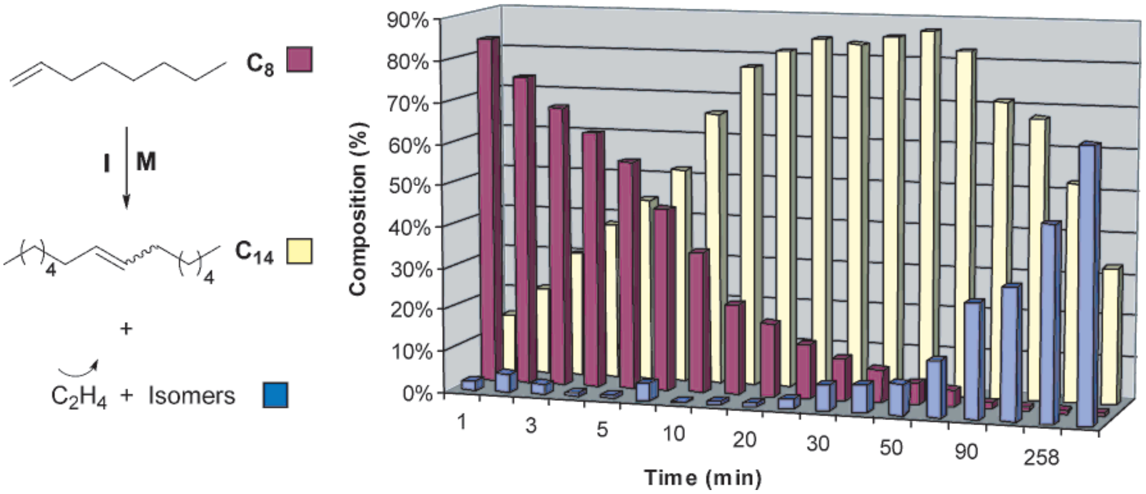

Figure 11. Composition of olefin mixture as a function of time for reaction of **3** with 1-octene at 30 °C.

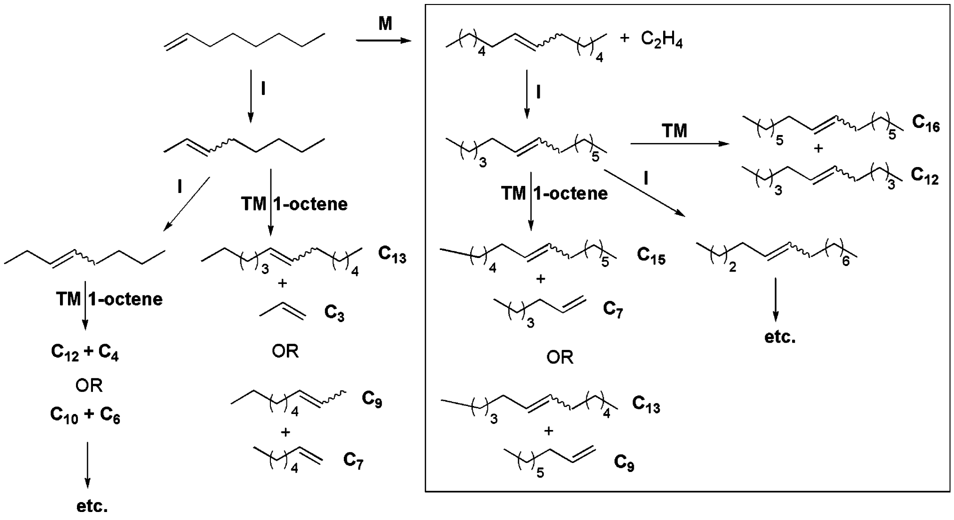

Figure 12. Proposed mechanism for isomerization of 1-octene.

If self-metathesis were the only mechanism operating in the presence of these catalysts, then this model reaction would yield 7-tetradecene exclusively (C_{14} in the figure above). Figure 11 shows that not to be the case, where the concentration of isomerized products increases at the expense of the product, 7-tetradecene, and the starting reagent, 1-octene. For example, exposure of 1-octene to complex **3** at room temperature leads to 94% conversion (1 h), where the product mixture consists of 82% 7-tetradecene and 18% isomers. By comparison, complex **2** is less active in this model study, requiring 3 days at room temperature to generate a similar conversion (86%). Complex **2** is slower to isomerize olefins, however, yielding a mixture containing only 3% isomers. Longer run times using complex **3** at room temperature result in considerably higher quantities of isomer content, up to 76% of the final product mixture. The starting reagent, 1-octene, is completely consumed, and the distribution of isomerized products (as determined by GC analysis) is centered about 7-tetradecene.

These observations are consistent with isomerization chemistry operating concurrently with metathesis, although at a slower rate than the initial condensation metathesis chemistry, which yields 7-tetradecene. In fact, three different reaction mechanisms operate concurrently throughout the conversion of 1-octene: condensation metathesis (we abbreviate this reaction as "M"), trans-metathesis (involving both internal double bonds and active metal alkylidene chain ends) (abbreviated "TM"), and isomerization chemistry (abbreviated "I") (Figure 12).

These three reactions compete until condensation metathesis is complete, after which only trans-metathesis (TM) and isomerization (I) continue. If the catalyst entities possess sufficiently long lives as appears to be the case for complex **3**, then the starting reagent, 1-octene, will be completely consumed, and an equilibrium mixture of isomerized products will result. Complex **5** approaches this situation, with conversions of 98% and a lower percentage of isomerization (23%) after 3 days. These results are consistent with the data of the kinetic study, and the product/isomer distribution indicates that isomerization occurs concurrently with metathesis. The relative rates of condensation metathesis, trans-metathesis, and isomerization apparently differ depending upon the identity of the metal catalyst complex, with isomerization being significantly slower than trans-metathesis and trans-metathesis being slower than condensation (end group) metathesis.

Since isomerization occurs at a slower rate than either metathesis reaction with complex **3**, lower temperatures should suppress this reaction to the advantage of metathesis chemistry. This has been shown to be true in prior research,[12] and the same observation is noted by us when using catalyst **3**. In fact, the conversion of 1-octene is quantitative at 0 °C in 3 days, with only 30% of the product mixture being isomers, as compared to 76% isomers at room temperature.

Recently, Mol et al. demonstrated that a possible decomposition pathway of catalyst **1** results in the formation of $(PCy_3)_2(CO)Ru(Cl)(Ph)$ which appears to be a good precatalyst for olefin isomerization.[19] This carbonyl complex could be converted into the corresponding hydride $(PCy_3)_2(CO)Ru(Cl)(H)$ upon reaction with a terminal olefin and could promote 1-octene isomerization without any trace of metathesis product. Further, Grubbs and co-workers witnessed the formation of the hydride complex $(H_2Mes)(PCy_3)(CO)Ru(Cl)(H)$ by heating complex **2** in the presence of oxygen-containing substrates.[20] These prior observations suggest that the ruthenium hydride equivalent of **3** could be formed under ADMET reaction conditions and could account for the isomerization chemistry reported herein. The rapid decomposition of complex **3** observed during our prior kinetic study is consistent with isomerization occurring early in the reaction and increasing over time, all as a result of increasing ruthenium hydride concentration. However, the possibility of isomerization catalyzed by the metathesis catalyst itself cannot be ruled out at this point.

Complex **3** is sufficiently active to induce isomerization of the starting reagent, 1-octene to other C_8 isomers (2-, 3-, and 4-octene), which happens concurrently with metathesis chemistry, and further, complex **3** appears to induce isomerization of internal bonds at a substantially higher rate than other catalysts.

Additional evidence for the high propensity of catalysts **3** and **5** to isomerize internal olefins is found in the melting behavior of the materials produced when using them to polymerize 1,9-decadiene. Schrock's molybdenum catalyst (complex **6**), which yields virtually no isomerization, produces poly(octenamer) that exhibits a melting point of 75 °C,[12] close to the theoretical maximum for this polymer. On the other hand, catalysts **3** and **5** yield poly(octenamer) samples possessing considerably lower melting points, 40 and 45 °C, respectively. Isomerization, in effect, creates random copolymers via migration of internal olefins along the polymer backbone or via monomer isomerization. This decrease in regioregular placement of olefinic groups in the poly(octenamer) results in a depression of the polymer peak melting point as observed for both catalysts **3** and **5**.

Conclusions

Complex **3** is highly active at low temperatures for the ADMET polymerization of 1,9-decadiene; loadings as low as 0.1 mol % produced high molecular weight poly(octenamer). In addition, complex **3** has the highest initiation rate of any phosphine ligated ruthenium complex to date. The catalyst is sensitive to thermal decomposition and therefore becomes less active as the temperature increases. The high initiation rate and activity at low temperatures make complex **3** an interesting prospect for further metathesis considerations, notably for low boiling point reagents or thermally sensitive substrates in both organic synthesis or polymerization. On the contrary, complex **4** does not exhibit satisfactory activity with nonfunctionalized substrates. Although known for its robustness, complex **4** appears to require stabilization either from a polar solvent or from a functionalized monomer in order to serve as a viable polycondensation catalyst. Complex **5** exhibits an interesting stability and produces high molecular weight polymers. The increase of steric interactions on the 4,5-dihydroimidazolylidene carbene ligand increases the catalytic activity, while the incorporation of Hoveyda-type ligand expands the stability of the complex.

Complexes **3** and **5** both catalyze olefin isomerization in high yields; however, given that both complexes are highly reactive at room temperature, their isomerization/metathesis processes can be mediated by lowering the reaction temperature. In fact, complex **3** efficiently metathesizes 1-octene at 0 °C, resulting in faster metathesis rates than isomerization. This isomerization pathway could be attributed to the hydride complex, whose formation and/or catalytic activity is highly dependent on temperature conditions. Therefore, increasing the catalyst stability toward decomposition seems most important to design catalysts that will produce regular polymers via metathesis chemistry. Nonetheless, complexes **3** and **5** are useful catalysts for ADMET polymerization, without the temperature constraints of either catalysts **1** or **2**.

Experimental Section

General Considerations. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of the ADMET polymers were recorded in $CDCl_3$ on either a Mercury series or Varian VXR-300 NMR superconducting spectrometer. Chemical shifts were referenced to residual $CHCl_3$ (7.23 for ^1H and 77.23 for ^{13}C) with 0.03% v/v TMS as an internal reference. All organometallic spectra were recorded in d_6-benzene, and the chemical shifts were referenced to residual C_6H_6 (7.16 for ^1H and 128.39 for ^{13}C).

Gel permeation chromatography (GPC) of the unsaturated ADMET polymers was performed using two 300 mm Polymer Laboratories gel 5 μm mixed-C columns. The instrument consisted of a Rainin SD-300 pump, Hewlett-Packard 1047-A RI detector (254 nm), TC-45 Eppendorf column heater set to 35 °C, and Waters U6K injector. The solvent used was THF at a flow rate of 1.0 mL/min. Polymer samples were dissolved in HPLC grade THF (approximately 0.1% w/v) and filtered before injection. Retention times were calibrated to polystyrene standards from Polymer Laboratories (Amherst, MA).

GC analysis was conducted on a Shimadzu GC-17A chromatograph equipped with a HP-5 (Hewlett-Packard) 25 m column with FID detection. All amounts of products were calculated by a systematic ratio to the decalin peak at 8.72 min, using the integrated peak areas.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min. Thermal calibrations were made using indium and freshly distilled *n*-octane as references for thermal transitions. Heats of fusion were referenced against indium. The samples were scanned for multiple cycles to remove recrystallization differences between samples, and the results reported are the second scan cycle. Reported values are given as T_m (melting peak).

Complex **4** was a gift from Materia Co. and was used as received. Complex **3** was synthesized according to the literature procedure.[6] All catalysts were stored in an argon-filled drybox prior to use in kinetic and polymerization experiments. 1,9-Decadiene (Aldrich) was distilled from Na/K alloy under reduced pressure into a Kontes flask equipped with a Teflon valve, degassed by three freeze−pump−thaw cycles, and stored in an argon-filled drybox. For the kinetic study, 1,9-decadiene was portioned into small Teflon-capped vials in the drybox and were removed and stored in a desiccator until use. All polymerizations were conducted in the bulk using the different monomer-to-catalyst ratio displayed in the tables. 2-Isopropoxystyrene was synthesized by a standard Wittig reaction on 2-isopropoxybenzylaldehyde using (methyl)triphenylphosphine iodide and potassium *tert*-butoxide (Aldrich). 2-Isopropoxybenzylaldehyde was synthesized via a Williamson ether synthesis from salicylaldehyde (Aldrich) and 2-bromopropane (Aldrich). Pentenyl ether was synthesized according to the literature,[21] distilled over CaH_2, and stored in the drybox. All other starting materials were distilled over Na/K alloy before use, except chlorinated compounds which were distilled over CaH_2. After distillation, d_6-benzene was degassed by three freeze−pump−thaw cycles and stored in an argon-filled drybox.

Synthesis of Complex 5. In a glovebox, complex **3** (930 mg, 1.00 mmol) and CuCl (Aldrich) (100 mg, 1.03 mmol) were weighed into a 100 mL Schlenk flask and dissolved in 20 mL of CH_2Cl_2. 2-Isopropoxystyrene (180 mg, 0.970 mmol) was dissolved in 2 mL of CH_2Cl_2 and added to the solution of complex **3** and CuCl at room temperature. The flask was equipped with a condenser, and the solution was refluxed for 20 min. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo to a green residue. The unpurified material was dissolved in a minimal volume of 1:1 pentane/CH_2Cl_2 and loaded onto a plug of silica gel. Insoluble copper−phosphine precipitates were removed prior to loading by passing the solution through a second Pasteur pipet containing a plug of glass wool. Elution with 1:1 pentane/CH_2Cl_2 removed a bright green band from the column. The eluant was concentrated, and addition of hexanes just prior to complete removal of the solvent resulted in spontaneous precipitation of the product. Filtration and drying under high vacuum afforded 691 mg (0.970 mmol, 97%) of a pale green powder. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 16.4 (s, 1H, Ru=C*H*Ph), 7.53 (t, 2H, *para* C*H*, $^3J_{H,H}$ = 7.2 Hz), 7.43 (m, 1H, *ortho* C*H*), 7.37 (m, 4H, *meta* C*H*), 6.80 (td, 2H, *meta−para* C*H*, $^3J_{H,H}$ = 7.4 Hz), 6.78 (d, 1H, *ortho* CH, $^2J_{H,H}$ = 8.4 Hz), 4.92 (sept, 1H, $(CH_3)C$*H*OAr, $^3J_{H,H}$ = 6.3 Hz), 4.18 (s, 4H, $N(CH_2)_2N$), 3.60 (sept, 1H, C*H*$(CH_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 1.38 (d, 6H, $OCH(CH_3)_2$, $^2J_{H,H}$ = 6.3 Hz), 1.26 (d, 24H, $CH(CH_3)_2$, $^3J_{H,H}$ = 7.1 Hz). ^{13}C NMR (C_6D_6, 75 MHz): δ = 296.7, 215.5, 149.6, 144.79, 130.0, 129.1, 124.8, 122.4, 122.2, 113.2, 112.1, 112.1, 75.2, 54.9, 29.3, 26.8, 23.9, 21.9.

Kinetic Study. The kinetic study was performed with the same apparatus and following the same procedure as previously described by Wagener.[11] Each catalytic run was repeated five times for reproducibility.

ADMET Polymerization of 1,9-Decadiene. All glassware was thoroughly cleaned and oven-dried. All metathesis reactions were initiated inside the drybox using 50 mL Schlenk flasks equipped with a Teflon stirbar. The flasks were then brought out of the drybox and placed on a high-vacuum line ($<10^{-3}$ mmHg) while vigorously stirring. The polymerization vessel was exposed to intermittent vacuum at room temperature until the reaction either became highly viscous or solid (stirring ceased). The flask was then placed in a 55 °C oil bath under high vacuum ($<10^{-3}$ mmHg) for 120 h. The polymerization vessel was cooled at room temperature, and finally, the unsaturated polymer was taken up into toluene and precipitated into cold acidic methanol (1 M HCl) to remove catalyst residue.

Self-Metathesis Dimerization. A clean, dry 50 mL Schlenk flask equipped with a Teflon stir bar was charged with complex **3** or **5** at the desired ratio in the drybox. The flask was brought out of the drybox and placed on a Schlenk line. Typically, 4.5 mmol of olefin was injected through an Ar-purged syringe. The mixture was stirred vigorously at the desired temperature under Ar and open to an oil bubbler to maintain ambient pressure. For complex **3**, samples were taken at appropriate intervals under a positive pressure of Ar with a dry pipet and added to a chloroform solution containing traces of 2,6-di-*tert*-butyl-4-methylphenol used as a radical inhibitor, ethyl vinyl ether used to quench the metathesis catalyst, and decalin used as a standard internal reference.

Measurement of the Thermal Stability of Complexes 3 and 5. Benzene-d_6 solutions (32 mM) of complexes **3** and **5** were heated to 55 °C and monitored by ^{1}H NMR spectroscopy. The half-life was calculated as the time required for half the material to decompose ($\tau_{1/2}$) through integration of the carbene peak (19.9 ppm for **3**, 16.4 ppm for **5**), which disappears with decomposition of the complex.

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Note Added after ASAP Posting

This article was released ASAP on 10/07/2003. In the Results and Discussion section, paragraph 13, text was deleted. The correct version was posted on 10/10/2003.

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